

JAPANESE

[JP,11-192777,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL  
FIELD PRIOR ART EFFECT OF THE INVENTION  
TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the recording sheet which records a picture (it is a concept also containing a character image) etc. using a color material. In order to form an image sheet by ink jet recording, thermal transfer recording, electrophotographic recording, etc. especially, it is related with the recording sheet used advantageously.

[0002]

[Description of the Prior Art]In recent years, the recording method and device which various information processing systems were developed and fitted each information system are also developed and adopted with rapid development of the information industry. It is known that the weight saving

of a device and miniaturization which the thermal-ink-transfer-printing recording method using an ink jet or the ink recording method using a plotter and a melting type color material, or a sublimated type color material uses are easy, and noise does not have them, either, and they are excellent also in operativity and conservativeness in such a recording method. By such a recording method, formation of a color picture is also easy. Also with the recording system of the conventional electrophotographing system, colorization progresses, and the printer and copying machine in which FURUKARA is possible have been developed and commercialized with high resolution.

[0003]Although various kinds of methods are developed as an inkjet method, There are three sorts, the method of using the coloring matter solution (water-based ink) which roughly divides and contains water soluble coloring matter, the method of using the coloring matter solution (oily ink) containing oil-soluble coloring matter, and the method of carrying out thermofusion of the low melting point solid wax (wax ink) containing coloring matter, and using it. The mainstream is a type which uses a water-based ink. Any method is the method of forming a picture by the method of solidifying ink by making the surface of an ink recording sheet breathe out the particle drop of ink, and performing desiccation or cooling after that.

[0004]A thermal-ink-transfer-printing method is roughly divided, and has two sorts of methods. The first method is the method (heat-of-fusion transfer) of making the ink sheet in which the ink layer of thermofusion nature was formed on the base material carrying out melting of the ink layer to pattern state by carrying out heat impression from the base material side at pattern state, making a recording sheet transferring the melted ink, and acquiring a picture.

The second method is the method (heat-of-sublimation transfer) of performing heat impression from the base material side to the thermal recording material in which the ink layer which consists of resin and the sublimability color of a high softening point was formed on the base material, like the former, making pattern state sublimating sublimation dye to it, making an ink image transferring on a recording sheet, and acquiring a picture.

After giving an optical image pattern to the electrified photoconductive layer in an electrophotographing system,

forming an electrostatic latent image and developing negatives with a toner subsequently, the method of transferring a toner image to a recording sheet and carrying out melting fixing of the toner with heat is in use.

[0005]On the other hand, it may be necessary to form a picture on a transparent sheet. In this case, a transparent picture is transferred on a transparent recording sheet using either of the above-mentioned methods using the bright film which provided the transparent color material acceptance (absorption) layer in the surface as a recording sheet. By forming a transparent picture on such a transparent recording sheet, the film for a back light display used instead of the OHP film and printing poster which are used instead of a slide, or the plotting board, for example, the film for mother prints, etc. are created.

[0006]The recording sheet (bright film) in which the picture (a transparent picture or a light transmittance state picture) was formed by the above-mentioned recording method, When acquiring the picture it is [ for the color material which needs to show hue, chroma saturation, and brightness excellent in the picture acquired and forms the picture further to have pasted up firmly on the surface of a recording sheet ] required it, and still more minute in the case of ink jet recording, Liquefied ink is absorbed early and it is required that neither an ink blot nor ink \*\*\*\*\* should be generated etc.

[0007]In order to solve these problems, various proposals are made from the former. For example, the recording sheet which becomes JP,57-14091,A and JP,61-19389,A from the hyaline layer of a transparent substrate, and colloidal silica and water soluble resin which were provided on it is proposed. However, since this hyaline layer has too large the particles of colloidal silica and there is too much quantity of water soluble resin, voidage big enough is not obtained, but for this reason, the above-mentioned recording sheet has the problem that an ink rate of absorption large enough is hard to be shown.

[0008]The recording sheet possessing the color material receiving layer which has the fine pores formed from quasi-boehmite particles is indicated by JP,2-276670,A and JP,3-281383,A. According to this invention person's examination, although this recording sheet showed high ink absorbency, since the refractive index was high, it became

clear that transparency high enough was not obtained.  
[0009]The recording sheet which has a hyaline layer which becomes JP,61-53598,A from a base material, and the particles and water soluble resin of synthetic silica and the refractive indices 1.44-1.55 which were provided on it further again is indicated. Synthetic silica has the primary particle diameter usually over 10 nm, and also an aggregated particle serves as particle diameter of several 100 nm. The recording sheet containing such particles does not show light transmittance high enough that such aggregated particles are easily scattered [ therefore ] about in light. Since a hyaline layer is a big aggregated particle and it has comparatively large holes, generating of an ink blot or ink \*\*\*\*\* cannot fully be prevented.

[0010]The recording sheet in which the color material receiving layer which has the three-dimensional structure of the high voidage formed in JP,7-276789,A from inorganic particles and water soluble resin as a recording sheet which solves the above-mentioned problem was provided on the transparent substrate is proposed. It is supposed that a picture enough control of the above-mentioned ink absorbency and a mixed-colors blot and high-resolution can be acquired by this composition.

[0011]

[Problem(s) to be Solved by the Invention]This invention primarily aims to provide the inorganic particles and water soluble resin in which high transparency and the outstanding color material stability are shown, or the recording sheet provided with the becoming color material receiving layer.

[0012]Generally, the inorganic particles used by the color material receiving layer of the high voidage formed from inorganic particles and water soluble resin have small particles, and their content of the particles in a color material receiving layer is also large. And when the coating liquid containing the material for forming such a color material receiving layer was applied, while drying the coating layer, it became clear by this invention person's examination that a cracking crack may occur. And especially this cracking crack became clear [ that it is also easy to generate when it dries at a comparatively high temperature ], in order to shorten drying time. Although the method of making viscosity of the binder of coating liquid comparatively high is proposed by JP,9-109545,A as a

method of preventing this cracking crack, since it is easy to generate application unevenness etc. and leads to the fall of the workability of spreading formation of a color material receiving layer in this method, it is not desirable. This method cannot be said to be enough in a cracking crack preventive effect.

[0013]In order to prevent a cracking crack of the above-mentioned color material receiving layer, this invention person repeated examination, and the cracking crack of a coating layer became clear [ generating at the stage to shift to decreasing drying ] in the middle of dry [ the ] (i.e., constant rate drying), after applying the coating liquid for color material receiving layer formation on a base material. Based on this knowledge, this invention person repeated examination further and completed the invention of the recording sheet which prepared it as soon as possible as raised the film strength of the coating layer in the state of the constant rate drying before a decreasing drying state starts. This invention is written in the Japanese-Patent-Application-No. No. 296285 [ nine to ] specification. Although the example which applied the silane coupling agent on the porous membrane, and gave the water resisting property was shown by this application, as a result of this invention person's repeating examination, also by applying dye mordant simultaneously with a cross linking agent, it found out that waterproof improvement was possible and this invention was reached.

[0014]Therefore, this invention can obtain an image sheet by ink jet recording, thermal transfer recording, or electrophotographic recording, and it also sets it as the purpose to provide the recording sheet which has the color material receiving layer excellent in the water resisting property which a cracking crack does not generate easily at the time of spreading desiccation, and can be formed simply.

[0015]Especially this invention can form a minute picture, without preventing the absorption nonuniformity of ink and generating an ink blot and ink \*\*\*\*\* by absorbing liquefied ink promptly. It aims at providing the recording sheet which fitted ink jet recording especially it had the color material receiving layer excellent in the water resisting property which can be formed simply, without a cracking crack occurring at the time of spreading desiccation.

[0016]

[Means for Solving the Problem] In a recording sheet in which a color material receiving layer is provided on a base material, this invention has this color material receiving layer in a recording sheet being a hardening layer of water soluble resin containing inorganic particles and dye mordant. This invention applies again coating liquid in which a color material receiving layer contains inorganic particles and water soluble resin on a base material, Before an applied layer comes to show the falling rate of drying simultaneously with the spreading, it is also in the above-mentioned recording sheet which is the layer obtained by giving and stiffening a solution containing a cross linking agent which can construct a bridge in water soluble resin, and dye mordant. Coating liquid in which, as for this invention, a color material receiving layer contains inorganic particles and water soluble resin again, It is also in the above-mentioned recording sheet which is the layer obtained by carrying out simultaneous spreading and making it harden on a base material where barrier liquid (however, either [ at least ] a solution containing a cross linking agent or barrier liquid is made to contain dye mordant) which consists a solution containing a cross linking agent of material which does not react to a cross linking agent is inserted.

[0017] The desirable mode of a recording sheet of this invention is as follows.

- (1) A cross linking agent is a boron compound (especially borax).
  - (2) Inorganic particles is [ primary / an average of / particle diameter ] silica particles of 20 nm or less (preferably 10 nm or less, especially the range of 3-10 nm).
  - (3) Water soluble resin is polyvinyl alcohol or gelatin.
  - (4) A weight ratio of inorganic particles and water soluble resin is in the range of 1.5:1-10:1 (inorganic particles: water soluble resin).
  - (5) A color material receiving layer has the voidage (especially voidage of 50 to 80%) of 40 to 80%.
- [0018] (6) A recording sheet is an object for ink jet recording.
- (7) Coverage on a color material receiving layer of a cross linking agent content solution is in the range of 0.01 - 10 g/m<sup>2</sup> (especially the range of 0.05 - 5 g/m<sup>2</sup>) by a cross linking

agent equivalent unit.

(8) A color material receiving layer has a three-dimensional network.

(9) A color material receiving layer has 30% or less of Hayes.

(10) The above-mentioned recording sheet for ink jet recording whose thickness of a color material receiving layer is 10-50 micrometers.

(11) An object for electro photography or the above-mentioned recording sheet for thermal recording whose thickness of a color material receiving layer is 0.1-10 micrometers.

(12) Dye mordant contained in a color material receiving layer is basic polymer.

[0019]

[Embodiment of the Invention]The recording sheet of this invention has the basic constitution which consists of a base material and a color material receiving layer formed on the base material, for example, can manufacture it as follows.

[0020]Opaque materials, such as paper, may be used as a base material, using transparent materials, such as a plastic, as a material which can be used. As for a base material, when employing the transparency of a color material receiving layer efficiently in this invention, it is preferred that they are a transparent substrate or an opaque base material of high gloss. As a material which can be used as a transparent substrate, it is transparent and the material which has the character to bear radiant heat when used on OHP or a back light display is preferred. As such a material, polyester; nitrocelluloses, such as polyethylene terephthalate, Cellulose ester, such as cellulose acetate and cellulose acetate butylate, and polysulfone, polyphenylene oxide, polyimide, polycarbonate, polyamide, etc. can be mentioned. Polyester is preferred in these and especially polyethylene phthalate is preferred. Although there is no restriction in particular about the thickness of a transparent substrate, it is easy to deal with a 50-200-micrometer thing, and desirable.

[0021]That in which the near surface in which a color material receiving layer is provided has not less than 40% of degree of brilliancy as an opaque base material of high gloss is preferred. The above-mentioned degree of brilliancy is a value calculated by measuring in accordance with the

method of a statement to JIS P-8142 (75-degree specular gloss test method of paper and a paperboard). As an example of the opaque base material of high gloss, art paper, coat paper, a cast-coated paper, Paper of high gloss, such as a baryta paper used for the base material for film photos, etc.; Polyester, such as polyethylene terephthalate (PET). Cellulose ester, such as a nitrocellulose, cellulose acetate, and cellulose acetate butylate. Or polysulfone, polyphenylene oxide, polyimide, polycarbonate, The film of the high gloss which made plastic films, such as polyamide, contain a white pigment etc., and was made opaque (a surface calendar process etc. are performed), Or the film etc. with which the enveloping layer of the polyolefine which contains a white pigment or is not contained was provided in the surface of content plastics, such as the various above-mentioned papers, the above-mentioned transparent plastic film, or a white pigment, can be mentioned. White pigment content foaming polyester film (calcium content foaming PET which made an example and polyolefine particles contain and formed the opening by extension) can also be mentioned. The special kind paper etc. in which the polyolefine coat paper (base paper etc. by which the white pigment content polyolefin layer was provided in the surface) currently generally used, or a metal deposition layer was provided can be conveniently used as a base material for film photos. The base paper in which especially the white pigment content polyolefin layer was provided, the polyester (preferably PET) film in which the white pigment content polyolefin layer was provided, white pigment content polyester film, or white pigment content foaming polyester film is preferred. Even if it attaches the thickness of an opaque base material, there is no restriction in particular, but it is easy to deal with a 50-200-micrometer thing, and desirable.

[0022]As a base material, what performed corona discharge treatment, flame treatment, and UV irradiation treatment may be used.

[0023]When the color material receiving layer of the recording sheet of this invention applies the coating liquid containing inorganic particles and water soluble resin on a base material, Before the applied this layer comes to show the falling rate of drying simultaneously with this spreading, it is preferred that it is the layer which the water soluble



resin obtained by giving and stiffening the solution containing a cross linking agent and dye mordant on a coating layer hardened by the cross linking agent.

[0024]The color material receiving layer of the recording sheet of this invention, The coating liquid containing inorganic particles and water soluble resin and the solution containing a cross linking agent, It can also obtain by carrying out simultaneous spreading and making it harden on a base material, where the barrier liquid (however, either [ at least ] the solution containing a cross linking agent or barrier liquid is made to contain dye mordant) which consists of material which does not react to a cross linking agent is inserted.

[0025]Polyvinyl alcohol (PVA) which is resin which has hydroxyl as a hydrophilic structural unit as an example of water soluble resin, Cellulose type resin [methyl cellulose (MC), ethyl cellulose (EC), ], such as hydroxyethyl cellulose (HEC) and carboxymethyl cellulose (CMC), Kitchens and starch; Polyethylene oxide (PEO) which is resin which has an ether bond, The polyacrylamide (PAAM) and the polyvinyl pyrrolidone (PVP) which are resin which has polypropylene oxide (PPO), polyethylene-glycol (PEG), and polyvinyl ether (PVE);, an amide group, and an amide bond can be mentioned. Polyacrylate, maleic acid resin, alginate, and gelatin which have a carboxyl group as a dissociative group can be mentioned.

[0026]As inorganic particles, a silica particle, colloidal silica, a calcium silicate, zeolite, kaolinite, halloysite, white mica, talc, calcium carbonate, calcium sulfate, boehmite, quasi-boehmite, etc. can be mentioned, for example. What has a refractive index in the range of 1.40-1.60 from the point of not reducing transparency is preferred. A silica particle is preferred in these. The first [ an average of ] particle diameter of inorganic particles has a common thing of 20 nm or less (preferably 10 nm or less, especially 3-10 nm), and, as for a refractive index, it is preferred that they are the 1.45 neighborhoods.

[0027]By the hydrogen bond by a surface silanol group, for an adhesion and cone reason, particles can form the structure where especially voidage is large, when especially the first [ an average of ] particle diameter is 10 nm or less as mentioned above, and the ink absorption feature of a silica particle improves. A silica particle is divided roughly

into wet process particles and dry method particles by a manufacturing method. The method of the acidolysis of a silicate generating active silica, polymerizing this moderately in wet process, carrying out flocking settling, and obtaining hydrous silica is in use. One dry method has a method in use of obtaining anhydrous silica by the method (arc process) of carrying out the heating reduction evaporation of the method (flame hydrolysis), the silica, and corks by elevated-temperature gaseous phase hydrolysis of halogenation silicon by an arc in an electric furnace, and oxidizing this with air. Although the density of a surface silanol group, the existence of a hole, etc. have a difference and character different, respectively is shown, voidage tends to form the high three-dimensional structure, and the hydrous silica and the anhydrous silica which are obtained by these methods have it, especially when it is a silicic anhydride (anhydrous silica). [ preferred ] Although this reason is not clear, when the density of a surface silanol group is hydrous silica, it is easy to condense many particles with 5-8-piece  $[\text{nm}]^{-2}$  densely (aggregate), It is presumed that it is because it becomes rough flocculation (flocculate) in the case of one anhydrous silica and it becomes the structure where voidage is high since it is small, 2-3-piece  $[\text{nm}]^{-2}$  and.

[0028]When the kind of resin combined with a silica particle is important and it uses anhydrous silica from a viewpoint of transparency, PVA, especially PVA of the degree of low saponification (the degree of saponification is 70 to 90% preferably) are preferred from a point of a light transmittance state as water soluble resin. Although PVA has a hydroxyl group in a structural unit, the three-dimensional network which makes the aggregated particle of a silica particle a chain unit is made easy for this hydroxyl group and the silanol group on the surface of a silica particle to form a hydrogen bond, and to form, and it is considered that the color material receiving layer of the structure where voidage is high is formed by this. Thus, not only the minute record which absorbs ink quickly according to capillarity, and has neither an ink blot nor ink \*\*\*\*\* is possible, but the obtained porous layer can paste up firmly the color material in thermal recording, and the toner in electrophotographic recording in ink jet recording. It is understood that this reason is because a color material and a

toner permeate in the fine pores of a porous layer, the geometrical anchor effect which originates in a three-dimensional network as that result occurs and this fixes a color material etc. firmly. Since the rate of inorganic particles increases, there is the feature that the embossing-proof nature in electrophotographic recording also has highly high heat resistance.

[0029]The ratio (PB ratio: weight of the inorganic particles to the weight 1 of water soluble resin) of inorganic particles (preferably silica particle) and water soluble resin has big influence also on the membrane structure of a color material receiving layer. If PB ratio becomes large, voidage, pore volume, and surface area (per unit weight) will become large. If PB ratio exceeds 10, there are not film strength and an effect over the cracking crack at the time of desiccation, on the other hand, by less than 1.5, an opening should be easily closed by resin, voidage will decrease, and ink absorption performance will fall. For this reason, the range of 1.5-10 is preferred for PB ratio. Like especially an OHP film, to touch the picture of a recording sheet directly by hand in many cases, the color material receiving layer needs to show sufficient film strength. In this case, as for PB ratio, it is preferred that it is especially five or less, and as for PB ratio, in order to acquire high-speed ink absorbency with an ink-jet printer, it is preferred that it is two or more, and it is preferred that it is especially in the range of 2-5.

[0030]For example, when the first [ an average of ] particle diameter carries out spreading desiccation of the coating liquid which distributed thoroughly [ PB ratio / 2-5 ] in solution anhydrous silica and water soluble resin of 10 nm or less, The three-dimensional network which makes the aggregated particle of a silica particle a chain unit is formed, average fine pores can form 30 nm or less, voidage can form 0.5 or more mL/g of fine-pores specific volume bulk, and specific surface area can form easily the porous membrane of the translucency more than  $100\text{-m}^2/\text{g}$  not less than 50%.

[0031]The color material receiving layer of the recording sheet of this invention is a layer which a cross linking agent and dye mordant were given to the layer (porous layer) which uses inorganic particles and water soluble resin as the main ingredients, and water soluble resin hardened by the cross linking agent. As for grant of a cross linking agent, it is preferred to be carried out before the coating liquid layer

for porous layer formation comes to show the falling rate of drying at the same time the above-mentioned coating liquid for porous layer formation is applied. The cracking crack generated by this operation while the coating layer of the coating liquid for porous layer formation dries can be prevented effectively. Namely, before a coating layer comes to show the falling rate of drying at the same time the above-mentioned coating liquid for porous layer formation was applied or, The film strength of a coating layer is immediately raised substantially by a cross linking agent content solution's permeating in a coating layer, reacting to the water soluble resin in a coating layer promptly, and making water soluble resin polymers-ize (hardening). As a result, the cracking crack generated at the time of desiccation of the coating layer of the above-mentioned coating liquid for porous layer formation can be prevented effectively.

[0032]As an example of the cross linking agent used for formation of the color material receiving layer of the recording sheet of this invention, borax, boric acid, and borate (an example and an orthoboric acid salt -- it  $\text{InBO}_3$  (ing),  $\text{ScBO}_3$  (ing) and)  $\text{YBO}_3$ ,  $\text{LaBO}_3$ ,  $\text{Mg}_3(\text{BO}_3)_2$ ,  $\text{Co}_3(\text{BO}_3)_2$  and diborate (an example and  $\text{Mg}_2\text{B}_2\text{O}_7$  --) [ 5 and ]  $\text{Co}_2\text{B}_2\text{O}_5$  and a metaboric acid salt (an example -- it  $\text{LiBO}_2$  (ing) and)  $\text{Ca}(\text{BO}_2)_2$ ,  $\text{NaBO}_2$ ,  $\text{KBO}_2$ , tetraborate (an example,  $\text{Na}_2\text{B}_4\text{O}_7$  and  $10\text{H}_2\text{O}$ ). 5 borate (an example,  $\text{KB}_5\text{O}_8$  and  $4\text{H}_2\text{O}$ , and  $\text{Ca}_2\text{B}_6\text{O}_{11}$  and  $7\text{H}_2\text{O}$ .)  $\text{CsB}_5\text{O}_5$ , glyoxal, melamineformaldehyde (an example, methylolmelamine, alkylation methylolmelamine), methylol urea, resole resin, polyisocyanate, etc. can be mentioned. Borax, boric acid, or borate is preferred in these. Since using it combining polyvinyl alcohol as water soluble resin causes crosslinking reaction promptly, borax, boric acid, and borate have it. [ preferred ]

[0033]When using gelatin as water soluble resin, the following compound known as a hardening agent of gelatin can be used as a cross linking agent. Aldehyde system compounds, such as formaldehyde, glyoxal, and a glutaraldehyde; Diacetyl, Ketone system compounds, such as cyclopentane dione; Bis(2-chloro ethylurea)-2-hydroxy-4,6-dichloro-1,3,5-triazine, Active halogen compounds,

such as 2,4-dichloro-6-S-triazine sodium salt; Divinylsulfonic acid, 1,3-vinylsulfonyl 2-propanol, a N,N'-ethylene screw (vinylsulfonyl acetamido), Activity vinyl compounds, such as 1,3,5-TORIAKURI roil hexahydro S-triazine; A dimethylolurea, N-methylol compound [, such as methyloldimethylhydantoin, ]; -- isocyanate system compound [, such as 1,6-hexamethylene diisocyanate, ]; -- U.S. Pat. No. 3017280. Aziridine system compound; indicated to 2983611. Ethyleneimino compound, such as epoxy compound; 1,6-hexamethylene N,N'-screw ethyleneurea, such as carboximide compound; glycerol triglycidyl ether indicated to U.S. Pat. No. 3100704; Mucochloric acid, halogenation carboxyaldehyde system compound [, such as mucophenoxy KURORU acid, ]; -- dioxane compound [, such as 2,3-dihydroxydioxane, ]; -- chromium alum, potash alum, zirconium sulfate, chromium acetate, etc. Two or more sorts can be combined and these hardening agents (cross linking agent) can also be used, even if independent.

[0034]The solution of a cross linking agent dissolves a cross linking agent in water and/or an organic solvent, and is prepared. As for the cross linking agent concentration in a cross linking agent solution, 0.05 to 10 % of the weight is preferred, and its 0.1 to 7 % of the weight is especially preferred. Generally as a solvent of a cross linking agent, water is used. As an organic solvent, if a cross linking agent dissolves, it can be used arbitrarily, For example, alcohol, such as methanol, ethanol, and isopropyl alcohol; Acetone, Ketone, such as methyl ethyl ketone; halocarbon system solvents, such as ether, such as aromatic solvent; tetrahydrofurans, such as ester; toluene, such as methyl acetate and ethyl acetate, and dichloromethane, etc. can be mentioned.

[0035]In this invention, the water resisting property is raised by applying dye mordant with a cross linking agent. If dye mordant is added to the coating liquid for porous layer formation, may produce condensation for the cationicity of the anion electric charge of the surface of inorganic particles, such as silica, and dye mordant, but. If each is prepared as an independent solution and the method of applying is used, there will be no worries about condensation of inorganic particles, such as silica, and the selection range of dye mordant will spread.

[0036]As dye mordant, an amide group, an imido group, the 1st class amino group, the 2nd class amino group, Are a compound to contain at least one sort of cation groups chosen from the 3rd class amino group, the 1st class ammonium salt group, the 2nd class ammonium salt group, the 3rd class ammonium salt group, and a quaternary-ammonium-salt group, and as the example, Polyvinylbenzyl trimethylammoniumchloride, polydiallyldimethylammoniumchloride, Polymethacryloyloxyethyl-beta-hydroxyethyl dimethylammoniumchloride, A poly dimethylaminoethyl methacrylate hydrochloride, polyethylene RENIMIN, Polyallylamine, poly allylamine hydrochloride, polyamide polyamine resin, cation-ized starch, dicyandiamide formalin condensate, dimethyl- 2-hydroxypropyl ammonium salt polymer, etc. can be mentioned. As for a molecular weight, 1000 to about 20000 are [ these compounds ] preferred. There is a tendency for a molecular weight to become insufficient [ less than 1000 / a water resisting property ], or more by 200000, viscosity becomes high and handling fitness becomes poor.

[0037]When the coating liquid (coating liquid for porous layer formation) which uses inorganic particles and water soluble resin as the main ingredients is applied on a base material when manufacturing the recording sheet of this invention, It is desirable to use the method of giving a cross linking agent so that this coating layer may not cause a cracking crack, raising the film strength of a coating layer promptly, and giving dye mordant simultaneously and raising a water resisting property. Or [ applying the solution which contains a cross linking agent and dye mordant actually simultaneously with spreading of the coating liquid which uses inorganic particles and water soluble resin as the main ingredients ] (in this case) It is desirable to make the barrier liquid which consists of material which does not react to a cross linking agent intervene between the solutions containing the coating liquid and the cross linking agent which use inorganic particles and water soluble resin as the main ingredients, and dye mordant. Or it may make barrier liquid contain dye mordant in this case, after applying the coating liquid which uses inorganic particles and water soluble resin as the main ingredients, it is desirable to use the method of giving the solution which

contains a cross linking agent and dye mordant promptly.  
[0038]Next, after applying the coating liquid (coating liquid for porous layer formation) which uses inorganic particles and water soluble resin as the main ingredients, before the coating layer comes to show the falling rate of drying, how to give the solution which contains a cross linking agent and dye mordant promptly is explained.

[0039]the coating liquid for porous layer formation -- an average of 1 -- adding the silica particle not more than order particle diameter 10nm underwater (an example.) A high velocity revolution wet colloid mill (an example, the Clare mix (made by M Technique Co., Ltd.)) is used ten to 20% of the weight, For example, after making it distribute for 20 minutes (preferably for 10 to 30 minutes) on condition of a 10000 rpm (preferably 5000-20000 rpm) high velocity revolution, It can obtain by adding a PVA solution (for example, it is set to PVA of about 1/3 weight of silica like), and also distributing on the same conditions as the above. Thus, the obtained coating liquid is homogeneity sol and can obtain the porous layer which has a three-dimensional network by forming this on a base material with the following coating method.

[0040]Spreading of the coating liquid for porous layer formation can be carried out by applying the coating liquid produced by adding a spray for preventing static electricity etc. further by request, for example on a base material (film). Spreading can be performed, for example with publicly known coating methods, such as an extrusion die coater, air doctor coater, bread coater, rod coater, knife coater, squeeze coater, a reverse roll coater, and bar coater.

[0041]After spreading of the coating liquid for porous layer formation, before the coating layer comes to show the falling rate of drying, the solution containing the cross linking agent and dye mordant of this invention is applied on a coating layer by the same method as the above-mentioned coating liquid for porous layer formation, it can dry and the color material receiving layer by which this invention was hardened can be obtained. The solution containing a cross linking agent and dye mordant may be given by methods, such as a spray.

[0042]Before the above-mentioned coating layer comes to show the falling rate of drying, it is for several minutes after immediately after spreading, and it usually shows the

constant rate of drying which is a phenomenon in which the content of the solvent in a coating layer decreases in proportion to time in the meantime. Time to show such the constant rate of drying is indicated in the chemical engineering manual (707-712 pages, the Maruzen Co., Ltd. issue, October 25, Showa 55).

[0043]After spreading of the coating liquid for porous layer formation, the color material receiving layer of the recording sheet of this invention is preferably manufactured by giving the solution containing a cross linking agent and dye mordant by methods, such as spreading or a spray, while this coating layer shows the constant rate of drying. Generally after-spreading desiccation of the coating liquid for porous layer formation is performed at 50-180 \*\* for 0.5 to 10 minutes (especially for 0.5 to 5 minutes). Although this drying time naturally changes with coverage, a mentioned range is suitable for it.

[0044]When the coating layer immerses the base material which has this coating layer in the solution which contains a cross linking agent and dye mordant within the period which shows the constant rate of drying in the coating layer of the coating liquid for porous layer formation, Or a cross linking agent and dye mordant can also be introduced into the coating layer of the coating liquid for porosity formation by carrying out spray coating of the solution containing a cross linking agent and dye mordant to a coating layer. Spreading of the coating liquid containing a cross linking agent and dye mordant is faced, Although publicly known coating methods other than the above-mentioned method, such as a curtain flow coater, an extrusion die coater, an air doctor coating machine, bread coater, rod coater, knife coater, squeeze coater, a reverse roll coater, and bar coater, can be used, It is preferred to use the method in which coater does not carry out direct contact to a coating layer using an extrusion die coater, a curtain flow coater, bar coater, etc.

[0045]The coverage on the color material receiving layer of the coating liquid containing a cross linking agent and dye mordant has the common range of 0.01 - 10 g/m<sup>2</sup> at cross linking agent conversion, and its range of 0.05 - 5 g/m<sup>2</sup> is preferred. Generally a coating layer is heated for 0.5 to 30 minutes at 40-180 \*\* after spreading of the coating liquid containing a cross linking agent and dye mordant, and desiccation and hardening are performed. It is preferred to



heat in 1 to 20 minutes at 40-150 \*\*. For example, when using borax and boric acid as a cross linking agent, it is preferred to perform heating at 60-100 \*\* for 5 to 20 minutes.

[0046]Next, how to apply the solution which contains a cross linking agent and dye mordant simultaneously with spreading of the coating liquid (coating liquid for porous layer formation) which uses as the main ingredients the inorganic particles and water soluble resin which are another formation methods of the color material receiving layer of the recording sheet of this invention is explained. This method can be obtained, when the coating liquid for porous layer formation carries out simultaneous spreading of the solution containing the coating liquid for porous layer formation, and a cross linking agent and dye mordant and stiffens it on a base material, as a base material is contacted. Simultaneous spreading of the solution containing the coating liquid for porous layer formation, and a cross linking agent and dye mordant can be performed with the coating method which uses an extrusion die coater and a curtain flow coater, for example, for example. Generally desiccation after simultaneous spreading (multistory spreading) is performed by heating a coating layer for 0.5 to 10 minutes at 40-150 \*\*, and a coating layer hardens. It is preferred to heat a hardening layer for 0.5 to 5 minutes at further 40-100 \*\*. For example, when using borax and boric acid as a cross linking agent, it is preferred to heat for 5 to 20 minutes at 60-100 \*\*.

[0047]When an extrusion die coater performs the above-mentioned multistory spreading, for example, layering is formed before two sorts of coating liquid moves to the delivery neighborhood of an extrusion die coater, i.e., a base material top. And since crosslinking reaction already occurs easily by the interface of a bilayer when the coating layer (layering) of a bilayer moves to a base material, it becomes easy to generate thickening by mixing of regurgitation coating liquid near the delivery of an extrusion die coater, and may interfere with spreading operation. Therefore, when performing the above-mentioned simultaneous spreading, it is preferred to apply it simultaneous three layers with spreading of the solution containing the coating liquid for porous layer formation, and a cross linking agent and dye mordant, as the barrier layer solution (interlayer

liquid) which consists of material which does not react to a cross linking agent further is made to intervene among both coating liquid. Barrier layer solution should just choose what does not react to a cross linking agent but can form liquid membrane. For example, solution and water containing a little water soluble resin (it is used as a thickener) which does not react to a cross linking agent can be mentioned. As an example of the polymer used in consideration of spreading nature, hydroxypropyl methylcellulose, methyl cellulose, hydroxyethyl methyl cellulose, a polyvinyl pyrrolidone, gelatin, etc. can be mentioned. This barrier layer solution can also be made to contain dye mordant as mentioned above.

[0048]The obtained color material receiving layer can raise surface smoothness, transparency, and film strength after spreading desiccation by letting between roll nips pass under heat pressing, for example using a super calender, gloss calender, etc. However, decline in voidage needs to perform such processing by setting up few conditions in order to reduce voidage (namely, in order for ink absorbency to fall).

[0049]Since the thickness of the color material receiving layer produced by performing it above needs to have the absorption capacity which absorbs all drops in the case of ink jet recording, it is necessary to determine this in connection with the voidage of a coat. For example, if ink quantity is a case where voidage is 60% in 8 nL(s)/mm<sup>2</sup>, not less than about 15-micrometer film is needed for thickness. As for a color material receiving layer, in the case of ink jet recording, when this point is taken into consideration, it is preferred to have the thickness of the range of 10-50 micrometers. In the case of thermal ink transfer printing or an electrophotographing system, since a color material or a toner is adsorbed on the surface, a thin film is enough, and as for a color material receiving layer, it is preferred to have 0.1-10-micrometer thickness.

[0050]A single material may be sufficient as the inorganic particles and water soluble resin which mainly constitute a color material receiving layer, respectively, and the mixed stock of two or more raw materials may be sufficient as them. The color material receiving layer may contain acid and alkali as various kinds of mineral and a PH regulator, in order to improve the dispersibility of particles in addition to it, although it mainly consists of the above-mentioned

inorganic particles and water soluble resin. Various kinds of surface-active agents may be used for the purpose of raising spreading fitness and surface quality. In order to control surface frictional electrification and peel charge, or in order to adjust surface electric resistance in a xerography, the metal oxide particle with a surface-active agent with ion conductivity or electron conductivity may be included. Various kinds of mat agents may be included for the purpose of reducing the surface friction characteristic. Various kinds of antioxidants, an ultraviolet ray absorbent, and singlet oxygen quencher may be included for the purpose of controlling degradation of a color material again. [0051] Undercoat may be provided on a base material for the purpose of improving an adhesive property between a color material receiving layer and a base material, or adjusting electrical resistance. A color material receiving layer may be provided in both sides of a base material, in order to provide only in one side of a base material and to control modification of curl of a recording sheet, etc. An antireflection film may be provided in order to improve a light transmittance state to the opposite side or both sides, when providing [ the case where it uses by OHP etc. ] a color material receiving layer only in one side of a base material.

[0052]

[Example]

[0053][Example 1] By the following method, the sheet provided with the color material receiving layer for ink jet recording was produced.

[0054]

[Table 1]

(1) The presentation of the coating liquid for porous layer (front [ bridge construction ] color material receiving layer) formation (all the values of the weight section which shows the loadings of all the following coating liquid express solid content or a nonvolatile matter)

\*\* An anhydrous silica particle (primary [ an average of ] particle diameter: 7 nm, 10 weight-section surface silanol group: 2-3-piece  $[\text{nm}]^2$ , refractive-index: 1.45, trade name: Aerosil 300 (product made from Japanese Aerosil))

\*\* Polyvinyl alcohol (the degree of saponification: 81.8% and 3.3 weight-section degree-of-polymerization: 4000, trade name: VA440 (made by Kuraray Co., Ltd.))

**\*\* Ion exchange water 136.0 weight sections[0055]\*\*** A silica particle is added in the ion exchange water (73.3 weight sections) of **\*\***, A high velocity revolution wet colloid mill (Clare mix (made by M Technique Co., Ltd.)) is used, the PVA solution (what was dissolved in remainder 62.7 weight section of ion exchange water) after making it distribute for 20 minutes on 10000-rpm conditions -- in addition -- it distributed on the same conditions as the above, and the coating liquid for porous layer formation was obtained.

[0056]The extrusion die coater was used for the surface of the 200-micrometer-thick laminated paper for the photographic printing papers, the above-mentioned coating liquid was applied by the coverage of 200cc/[m ]<sup>2</sup>, and it dried for 3 minutes at 80 **\*\*** (3 m/second wind speed) with hot air drying equipment. The coating layer showed this period and the constant rate of drying. After the desiccation for these 3 minutes, promptly, the borax content solution of following (2) was made to immerse this coating layer for 1 second, and it dried for 10 minutes at 80 **\*\***. Thereby, dry membrane thickness formed the color material receiving layer which is 27 micrometers.

[0057]

[Table 2]

(2) borax content solution **\*\* borax 1 weight-section \*\*** surface-active agent 0.2 weight section (trade name: F-144D, Dainippon Ink & Chemicals, Inc. make)

**\*\* Diaryl dimethylammoniumchloride and diacid-izing 1.4 weight sections Sulfur copolymer \*\* ion exchange water 97.4 weight sections[0058][Example 2]** In the borax content solution of Example 1, the ink jet recording sheet was similarly produced instead of diaryl dimethylammoniumchloride and sulfur dioxide copolymer except having used polyallylamine.

[0059][Example 3] In the borax content solution of Example 1, the ink jet recording sheet was similarly produced instead of diaryl dimethylammoniumchloride and sulfur dioxide copolymer except having used dimethyl- 2-hydroxypropyl ammoniumchloride polymer.

[0060][Example 4] The ink jet recording sheet was produced by the following method.

[0061]

[Table 3]

Coating liquid \*\* hydroxypropyl methylcellulose for interlayer formation 5.5 weight sections (\*\*\*\*\*-\*\* 90SH; viscosity great 100000) \*\* (made by Shin-Etsu Chemical Co., Ltd.) surface-active agent (trade name: made by F-144D 2.0 weight-section Dainippon Ink & Chemicals, Inc.) \*\* Ion exchange water 992.5 weight sections[0062]In

Example 1, the coating liquid for porosity formation and simultaneous three layers of cross linking agent solutions were applied by making the above-mentioned coating liquid for interlayer formation into an interlayer. An extrusion die coater with the delivery of three slits is used, From the side which touches a base material, simultaneous three layers were applied by the coverage of coating liquid 200 cc/m<sup>2</sup> for porosity formation, coating liquid 30 cc/m<sup>2</sup> for interlayer formation, and cross linking agent solution 15 cc/m<sup>2</sup>, and it dried for 10 minutes at 80 \*\*. Thereby, thickness formed the color material receiving layer which is 27 micrometers.

[0063][Comparative example] In Example 1, except that a borax content solution did not contain diaryl dimethylammoniumchloride and sulfur dioxide polymer, the ink jet recording sheet was produced similarly.

[0064][Evaluation of an ink jet recording sheet] The ink jet recording suitability was evaluated by the following measuring methods about the ink jet recording sheet obtained above.

(1) Parallel ray transmissivity was measured using the Hayes hazemeter (HGM-2DP; made by Suga Test Instruments Co., Ltd.), and Hayes was measured. Hayes was measured using the recording sheet produced by forming a color material receiving layer on a 100-micrometer-thick polyethylene terephthalate film instead of the laminated paper for the photographic printing papers used as a base material in each example and a comparative example, in order to make the measurement easy.

[0065](2) The average value was calculated by having measured using the voidage mercury porosimetry (trade name: pore sizer 9320-PC2, Shimadzu Make), and having acquired voidage distribution.

(3) About degree-of-brilliancy each recording sheet, the degree of brilliancy was measured in accordance with the method of a statement to JIS-P-8142 (75-degree specular gloss test method of paper and a paperboard).

[0066](4) With an ink-absorption-velocity ink-jet printer

(trade name: PM-700C, made in SEIKO EPSON). Y (yellow) to a recording sheet, M (magenta), C (cyanogen), K (black), B (blue), G (green), and R (red) carried out solid printing, the contact press of the paper was carried out just behind that (after about 10 seconds), and it judged as follows by the existence of the transfer to the paper of ink.

AA: Some ink was not transferred by paper.

CC: Some ink was transferred by paper.

[0067](5) Generating each recording sheet of the cracking crack was observed visually, and it evaluated as follows according to the existence of the cracking crack generated on the surface, and its size.

AA: CC as which a cracking crack of the length which is BB:1-2mm as which a cracking crack is not regarded is regarded: A cracking crack of a length of not less than 3 mm is seen. [0068](6) The printing pattern same on a recording sheet was made to form using the same printer as measurement of a waterproof ink rate of absorption, and it dipped underwater for 1 minute after 3-hour neglect, and the flow condition of ink was observed visually and evaluated as follows.

AA: -- BB: into which a color did not flow at all -- CC:color to which a color flows on the whole and the depth of shade is thin is flowing nearly thoroughly [0069]The result of the above-mentioned evaluation is shown in the 1st following table.

[0070]

[Table 4]

1st Table. -----. Hayes Voidage

Degree of brilliancy Ink Cracking crack a water resisting property -- (%) (%) (%) Rate of absorption .

-----. Example 1 12.1 62 52 AA

AA AA example 2 11.9 60 53 AA AA AA example 3 11.8

61 50 AA AA AA example 4 11.2 61 51 AA AA AA.

----- comparative example 12.0 61

52 AA AA BB -----[0071]

[Effect of the Invention]The recording sheet provided with the color material receiving layer of this invention, Especially in ink jet recording, liquefied ink is absorbed early, and the high-definition picture excellent in the water resisting property can be formed simply, without a minute picture without an ink blot or ink \*\*\*\*\* not only being able to obtaining, but causing generating of the cracking

crack by the color material receiving layer which is a porous layer. Since it excels in the absorptivity of the color material receiving layer of the record sheet of this invention, and blot prevention, also in the various recording methods of thermal transfer recording or electrophotographic recording, the adhesive property of a color material or a toner improves. Therefore, it can be said that the recording sheet of this invention is a recording sheet which fitted various record methods and was excellent in productivity.

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[Translation done.]

